Dynamic Behaviour of Tris(2-methylallyl)chromium − NMR and DFT Results

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The variable-temperature ^{1}H NMR spectra of paramagnetic (2-Me-allyl)$_3$Cr in [D$_8$]toluene were recorded in the temperature range from 243 to 323 K. The changes observed in the spectra are interpreted in terms of intramolecular dynamic behaviour. Line-shape analyses gave an entropy of activation $\Delta H^{\ddagger}$ of 40(5) kJ/mol, and an entropy of activation $\Delta S^{\ddagger}$ of –31(4) J/mol·K for the observed transformation. This corresponds to a free energy of activation $\Delta G^{\ddagger}$ of 49(6) kJ/mol at 300 K. Different possible mechanisms were investigated by DFT. The presence of two different conformers, which were converted into each other by rotation of one allyl ligand around the allyl–chromium axis, may explain the observations.

Introduction

Homoleptic allyl complexes of the early transition elements (Groups 4−6) were prepared for the first time in the 1960s.[1] The complexes can act as one-component catalysts for polymerisation of 1-olefins and α,ω-dienes, both in homogeneous solutions and as deposits on oxide supports.[2] Despite their practical potential, the molecular structures of these complexes have not been determined experimentally, which is mostly due to their thermal instability. One property that has been widely studied for the Group 4 allyl complexes is the "rotation" of the allyl ligand that interchanges the *syn* and *anti* protons.[3] The activation energy for this transformation is typically found to be in the range 40 to 60 kJ/mol using variable-temperature NMR.

The Cr^{III} complex Cr(C$_3$H$_5$)$_3$ is paramagnetic, and has therefore not been analysed properly by NMR methods. An early crystal structure has been reported;[4] unfortunately, the quality of the data did not allow detailed structural information to be deduced, but the gross picture is a molecule with close to C_3 symmetry and close to trihapto-bonded allyl ligands. We recently reported the molecular structures of both Cr(allyl)$_3$ and Cr(2-Me-allyl)$_3$ from DFT calculations.[5] Both these molecules have C_{3h} symmetry. The dimeric Cr^{II} complex Cr$_2$(C$_3$H$_5$)$_4$, prepared by thermal decomposition of Cr(C$_3$H$_5$)$_3$, has been fully characterised by single-crystal X-ray diffraction;[6] it is diamagnetic and has thus also been characterised by ^{13}C NMR.[7]

In the present paper we report the observed high-power ^{1}H NMR spectra of (2-Me-allyl)$_3$Cr, dissolved in deuterated toluene, in the temperature range from −60 to +40 °C. From line-shape analysis, we have deduced the kinetic parameters for the transformation observed and we have used DFT calculations to test possible mechanisms that can explain the observed dynamics.

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Results and Discussion

^{1}H NMR spectra recorded at different temperatures are shown in Figure 1. Except for a strong signal at $\delta \approx 0$ (not shown), no other signals, other than those shown in Figure 1, were observed in the range from $\delta = -5000$ to +5000. The signal at $\delta \approx 0$ results from the diamagnetic species present: the protons of the imperfectly deuterated solvent, residual pentane, and 2,5-dimethylhexa-1,5-diene, formed as a by-product during the synthesis. At low temperatures, there are three broad signals at $\delta \approx 70$, 85, and 160, with relative peak areas of roughly 1:2:3.

Normally, one would assign these three peaks to the three symmetrically independent protons present: the protons of the methyl groups, the *syn* protons and the *anti* protons. As the temperature increased, there seemed to be a coalescence of all peaks at approximately 295 K. The fact that all observed protons ended up being magnetically equivalent, indicates that either a facile proton exchange was taking place in the complex, or that our first interpretation is wrong. NMR signals from paramagnetic species are notoriously difficult to assign, and some peaks might not be observable due to extreme broadening by the paramagnetic centre present. If the latter were the case, the protons closest to the chromium atom would be most heavily influenced by the paramagnetic effect; hence, their resonances could be expected to be undetectable. An alternative assignment of the three peaks could then be that the three peaks stem from three individual methyl groups or from three different individual protons of the methyl groups. In either case, all protons of the methyl groups become equivalent at elevated

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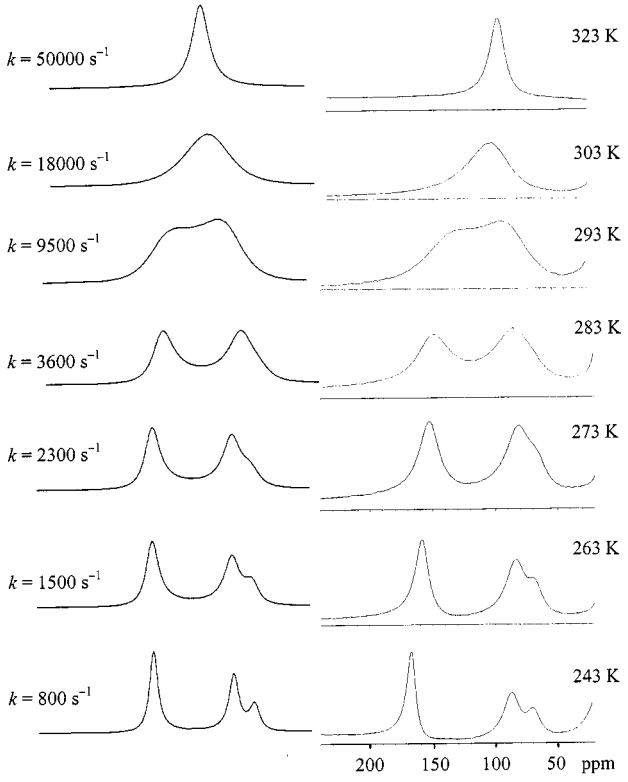


Figure 1. Experimental (right column) ^{1}H NMR spectra of (2-Me-allyl)$_3$Cr recorded in [D$_8$]toluene at the temperatures indicated; on the left are the modelled spectra shown with the corresponding rates

temperatures. Non-equivalent methyl groups can indicate that more than one conformation is present.

As noted above, NMR spectroscopy often gives little information on the structure of organometallic Cr^{III} complexes due to extreme line broadening.[8] The half-width of the peaks observed at low temperatures are large, the narrowest peak at $\delta = 160$ having a half-width of about 2400 Hz at 243 K, which is at the lower end of the estimated range suggested for Cr^{III} species (3000−25000 Hz at 500 MHz).[9] The enhancement of the nuclear longitudinal relaxation rate due to dipolar coupling to unpaired electrons is proportional to r^{-6}. The distance between the paramagnetic centre and the allylic protons is about 73% of the average distance to the methyl protons, meaning that the expected half-width of the allylic protons will be around 16000 Hz (80 ppm). Possible fluxional behaviour might increase the half-width further, and consequently the peaks would easily go into the background and thus remain unobserved. In addition, Cr(allyl)$_3$ does not give any peaks in the range from $\delta = -300$ to 300, which is a further indication that the allylic protons were not observed within this range for (2-Me-allyl)$_3$Cr.

The calculated structure of the tris(2-methylallyl)chromium molecule, structure **1** on the left in Figure 2, has been reported earlier.[5] It has C_{3h} symmetry and a ^{4}A′ electronic ground state, and in the following, its energy will be taken as the zero reference.

One might envisage three different interpretations of the observed NMR spectra:

A. Proton transfer from a methyl group to a terminal CH_2 group. The transfer may be either intra-allylic, or it may be a concerted mechanism involving all three allyl ligands.

B. Rotation of the allyl groups around the allyl−chromium axis. Actually, if we only observe the methyl groups, rotation around the allyl−metal axis cannot be separated, mechanistically, from the *syn*/*anti* exchange described in the introduction. Both routes were examined.

C. Rotation of the methyl groups.

Reaction path A may include an intermediate in which a hydrogen atom is removed from the methyl group of a 2-methylallyl ligand, giving an intermediate having both a hydrido and a trimethylenemethane ligand. For simplicity, the latter will be called corvyl[10] in the following discussion. This reaction path is shown as (i) in Figure 2. The intermediate, (corvyl)(hydrido)bis(2-methylallyl)chromium (**2**) was calculated to be as much as 105 kJ/mol higher in energy than its homoleptic allyl analogue. The distance between the hydrido ligand and one carbon atom of the corvyl ligand was chosen as a reaction coordinate for the reconstruction from (corvyl)(hydrido) to homoleptic triallyl. A transition state was found to be only 11 kJ/mol higher in energy than the (corvyl)(hydrido) intermediate, with a C−H distance of 1.66 Å. The complete exchange of a hydrogen atom requires the formation of (corvyl)(hydrido), then a 120° rotation of the corvyl ligand, followed by the reconnection of the corvyl and the hydrido ligands to a 2-methylallyl ligand. The exchange transforms a methyl group into a CH_2 group and at the same time transforms a CH_2 group into a methyl group. The activation energy of 116 kcal/mol is too high for reaction (i) to take place within the NMR timescale at the temperature in question, and hence other reaction paths must be investigated.

One could envisage a concerted transfer of hydrogen atoms between all three methylallyl groups. Structural optimisations were attempted in which all C−H distances for the transferring hydrogen atoms were constrained to be equal; the starting geometry is shown in Scheme 1. These attempts were fruitless, as they invariably converged to unphysical geometries of very high energies (> 250 kJ/mol). We therefore concluded that a proton transfer between the methyl group and the CH_2 group of the allyl ligand has too high a barrier, and thus cannot be used to explain the dynamics in the observed ^{1}H NMR spectra.

Our suggested mechanisms B and C are both based on the assumption that the allylic protons of the ligands are unobserved. Mechanism B concerns a rotation of one of the allyl ligands as shown as route (ii) in Figure 2. In the ground-state geometry all the methyl groups are connected by symmetry, and are thus expected to give only one peak in the ^{1}H NMR spectrum. However, by rotating one allyl group around the allyl−chromium axis by approximately 180°, a conformer is obtained in which all three methyl groups are, in principle, non-equivalent. This conformer **3** is expected to give three signals in the NMR spectrum, and

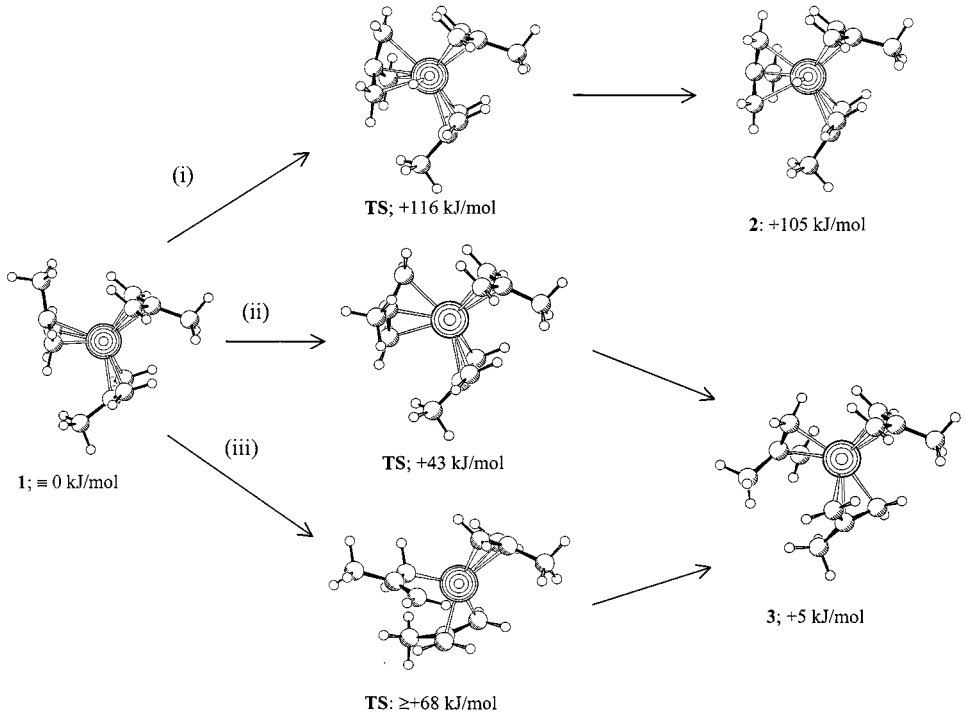
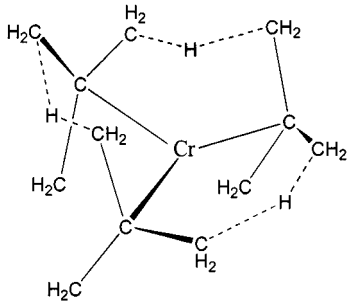


Figure 2. The structures and energies of central species and transition states (TS) obtained from DFT calculations: (i) transformation of one allyl ligand into a hydrido(trimethylenemethyl) complex; (ii) pure rotation of one allyl ligand around the allyl−chromium axis; (iii) $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ transformation leading to the same conformer as route (ii); see text for more details



Scheme 1

the energy is only 5 kJ/mol higher than the ground-state geometry. The rotation goes through a transition state, the structure of which is shown in the centre of Figure 2, with a relative energy of 43 kJ/mol. Considering the accuracy of the DFT energies, it is reasonable to suggest that both conformers are present at low temperatures. A possible interpretation of the observed ^{1}H NMR spectra is then that the high-symmetry conformer **1** gives rise to the single peak at $\delta = 160$, while the two broad peaks at $\delta = 70$ and 87, of different intensities, are due to the three methyl peaks of conformer **3**. For the latter conformer there is an additional fluxionality due to the flipping of two methyl groups having van der Waals contacts from side to side. The barrier for this flipping was estimated from DFT modelling to be 8 kJ/mol. This is below the detection limit in the NMR experiment. At elevated temperatures, the rotation of the allyl groups becomes rapid, interchanging the two conformers rapidly at the NMR time scale, leaving only one single methyl peak at temperatures above 300 K. A rough lineshape analysis was carried out in order to estimate the activation energy for the rotation process assuming two different species, one species with nine magnetically equivalent protons, and a second species containing three magnetically inequivalent sets of protons. The modelled spectra are given on the left-hand side in Figure 1. From the analyses we obtained an enthalpy of activation $\Delta H^{\ddagger}$ of 40(5) kJ/mol and an entropy of activation $\Delta S^{\ddagger}$ of −31(4) J/mol·K, corresponding to a free energy of activation $\Delta G^{\ddagger}$ of 49(6) kJ/mol at 300 K. The equilibrium constant for the transformation **1** $\rightleftarrows$ **3** was estimated to be 1.2(1). The DFT activation barrier obtained is within the error of the experimental value.

Actually, another mechanism leading to **3** could include a pseudo-rotation that interchanges the (assumed unobserved) *syn* and *anti* protons of the allyl ligand. Such a "rotation" is believed to proceed first by transferring the η^3-allyl ligand into an η^1-bonding mode, followed by a rotation around the $C_\alpha-C_\beta$ bond, and finishing by re-transferring the allyl ligand into an η^3-bonded mode. Setting the $Cr-C_\alpha-C_\beta-C_{(methyl)}$ dihedral angle equal to 180°, and minimising all other degrees of freedom, we found a DFT energy of 69 kJ/mol. This energy, which may be regarded as

a lower limit for the reaction barrier, is significantly higher than the pure rotation around the allyl−metal axis. We infer that the latter mechanism will dominate over the former.

The last possibility that should be considered is mechanism C, rotation of the methyl groups. Methyl rotations are, in most cases, unobserved by dynamic NMR due to the low energy barrier. However, one might speculate if steric requirements and/or the paramagnetism and consequently large shift differences could lead to observable methyl rotations. DFT calculations give a barrier of 7 kJ/mol for the methyl rotation in the high-symmetry ground-state conformer, which is too low when compared to the experimental value.

Conclusions

The observed line widths in the ^{1}H NMR spectra of tris(2-methylallyl)chromium are in accordance with what one would expect from Cr^{III} complexes. The estimated free energy of activation deduced from line-shape analysis of the NMR spectra, 49(6) kJ/mol, is in accordance with a mechanism where two conformers are present, and the conformers can be transformed into one another by rotation of one allyl ligand around the allyl−chromium axis. The other mechanisms investigated by using DFT calculations all have energies that are discrepant with the experimental results. However, we can only explain our observations by assuming that the terminal allylic protons are not observed in the spectra. This assumption is reasonable in light of the close distances between these protons and the paramagnetic metal centre.

Experimental Section

Experimental Details: Tris-(2-methylallyl)chromium [(2-$CH_3C_3H_4)_3Cr$] was prepared according to known procedures.[11] The complex could be stored as a 0.050 M pentane solution (determined by ICP) at −40 °C for at least two weeks. All handling of the complex was carried out at temperatures below −20 °C under argon. NMR samples were prepared by transferring 0.5−1.0 mL of the pentane solution to an NMR tube connected to an argon/vacuum line. The pentane was removed at approximately −30 °C under reduced pressure. Then, 0.5 mL of [D_8]toluene was distilled into the NMR tube, which was kept in liquid nitrogen until it could be sealed. Before the tube was introduced into the NMR magnet, the solution was allowed to thaw at −78 °C in a dry-ice/ethanol bath. The NMR measurements were performed with a Bruker DMX 200 Avance spectrometer operating at 200 MHz. A high-power ^{1}H NMR probe was utilised to achieve a spectrum over a wide frequency range. The probe was capable of producing 90° radio frequency (rf) pulses as short as 1.5 ms. In the present experiments, a more moderate pulse power of approx. 3 ms 90° pulse was utilised. A pulse length of 1.2 ms was used, corresponding to approximately 40°. The sweep width was set to 1.3 MHz, the repetition time was 3.02 s, and 96 scans were acquired in every experiment. A 0.6 ms dead time was allowed between pulse and acquisition, and the acquisition time was 19.4 ms. Line-shape analysis was carried out using the program WINDNMR.[12] Due to a software limitation in the maximum possible natural half-width of the peaks, only spectra in the temperature range 263 to 303 K were used in the analysis.

Computational Details: The DFT calculations were carried out using the program system ADF, developed by Baerends et al.[13] The frozen-core approximation was used for all atoms except hydrogen, keeping the orbitals up to and including 2p for chromium and 1s for carbon frozen in their atomic shapes. The orbitals were described by Slater-type orbital (STO) basis sets. The number of unfrozen basis functions, in order of increasing angular momentum, was (5,3,3) for chromium, (2,2,1) for carbon, and (2,1) for hydrogen, yielding TZVP quality for Cr and DZVP for C and H (note that for Cr, the number of unfrozen orbitals is larger than the number of valence orbitals). Slater exchange and the VWN parameterisation of the LDA correlation energy,[14] with the gradient corrections of Becke[15] for exchange and of Perdew[16] for correlation, were used for the exchange-correlation energies; the gradient corrections were added self-consistently. The accuracy of the numerical integration was set to $10^{-6.0}$, which may be assumed to give a numerical noise level of less than 0.1 kcal/mol in the final energies.[17] The calculations were carried out while making no initial assumptions of molecular symmetry. The calculations were run without restrictions, with separate sets of Kohn−Sham orbitals for each spin. No vibrational spectra have been computed.

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